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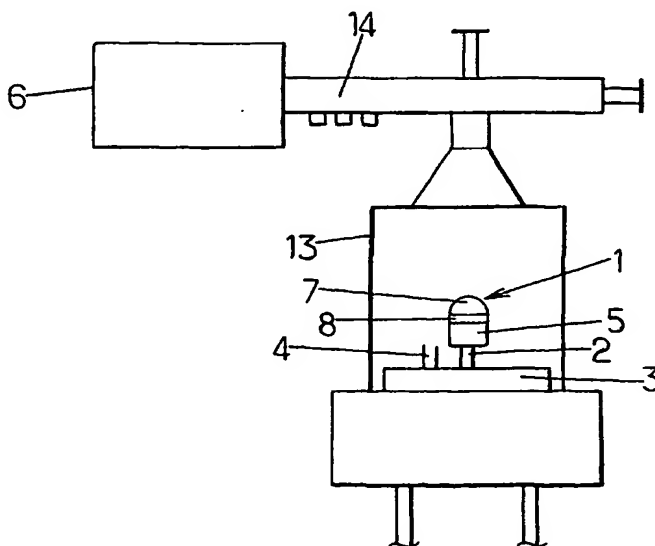
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[Continued on next page]

- (54) Title:** HIGH-SPEED DIAMOND GROWTH USING A MICROWAVE PLASMA IN PULSED MODE



- (57) Abstract:** Method for manufacturing a diamond film of electronic quality at a high rate using a pulsed microwave plasma, in which, in a vacuum chamber, a plasma of finite volume is formed near a substrate by subjecting a gas containing at least hydrogen and carbon to a pulsed discharge, which has a succession of low-power states and of high-power states, and having a peak absorbed power P_c , so as to obtain at least carbon-containing radicals in the plasma and to deposit the said carbon-containing radicals on the substrate in order to form a diamond film thereon. Power is injected into the volume of the plasma with a peak power density of at least 100 W/cm^3 , while maintaining the substrate to a substrate temperature of between 700°C and 1000°C .



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HIGH-SPEED DIAMOND GROWTH USING A MICROWAVE PLASMA
IN PULSED MODE

5 The present invention relates to a method for manufacturing diamond using a pulsed microwave plasma.

Current methods for manufacturing diamond films by microwave-plasma-assisted chemical vapour deposition
10 (MP-CVD) are of limited effectiveness since the large amounts of energy needed to obtain diamond of electronic quality at reasonable growth rates (about 2 $\mu\text{m}/\text{h}$) lead to heating of the walls on which hydrogen atoms contained in the plasma, that activate the
15 reaction, recombine and therefore cannot participate in the reaction. It is therefore necessary to install a constricting device for cooling the walls. In the proceedings of the Electrical Chemical Society (ECS) meeting held in San Francisco in 2001, it was proposed
20 in "*Diagnostics and modelling of moderate pressure microwave H_2/CH_4 plasmas obtained under pulsed mode*" by a number of co-inventors to use a periodic pulsed discharge with a low duty cycle (the ratio of the time during which energy is emitted to the period of the
25 discharge), in order to reduce the wall temperature, which is related to the average injected power, and therefore the recombination of hydrogen taking place thereon. Using such a pulsed discharge makes it possible to maintain a high temperature of the plasma,
30 which is related to the power injected during the pulse, and therefore to obtain a higher concentration of hydrogen atoms in the plasma. Thus, a diamond film may be deposited at a higher rate for constant consumed power.

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The invention relates to a method of this type in which, in a vacuum chamber, a plasma of finite volume is formed near a substrate by subjecting a gas containing at least hydrogen and carbon to a pulsed

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discharge, which has a succession of low-power states and high-power states, and having a peak absorbed power P_c , so as to obtain at least carbon-containing radicals in the plasma and to deposit the said carbon-containing radicals on the substrate in order to form a diamond film thereon.

The object of the present invention is to further improve these methods, especially their efficiency.

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For this purpose, the invention provides a process for manufacturing a diamond film assisted by a pulsed microwave plasma, which, apart from the abovementioned features, is characterized in that power is injected into the volume of the plasma with a peak power density of at least 100 W/cm^3 while maintaining the substrate to a substrate temperature of between 700°C and 1000°C .

By virtue of these arrangements, it is possible to obtain rapid growth of a diamond film, especially of electronic quality, on the substrate.

In preferred embodiments of the invention, one or more of the following arrangements may optionally be furthermore employed:

- a plasma having at least one of the following features is generated near the substrate:

· the pulsed discharge has a certain peak absorbed power P_c and the ratio of the peak power to the volume of the plasma is between 100 W/cm^3 and 250 W/cm^3 ,

· the maximum temperature of the plasma is between 3500 K and 5000 K ,

· the temperature of the plasma in a boundary region of the plasma located less than 1 cm from the surface of the substrate is between 1500 K and 3000 K and

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the plasma contains hydrogen atoms having a maximum concentration in the plasma of between 1.7×10^{16} and $5 \times 10^{17} \text{ cm}^{-3}$;

- said gas contains carbon and hydrogen in a carbon/hydrogen molar ratio of between 1% and 12%;

- said gas contains at least one hydrocarbon and a plasma having a concentration of the carbon-containing radicals of between $2 \times 10^{14} \text{ cm}^{-3}$ and $1 \times 10^{15} \text{ cm}^{-3}$ is generated;

- a pulsed discharge is produced, in which the ratio of the duration of the high-power state to the duration of the low-power state is between 1/9 and 1;

- at least one of the following parameters is estimated:

• a substrate temperature,

• a temperature of the plasma,

• a temperature of the plasma in said boundary region, located less than 1 cm from the surface of the substrate,

• a concentration of atomic hydrogen in the plasma,

• a concentration of carbon-containing radicals in the plasma,

• a concentration of carbon-containing radicals in said boundary region close to the plasma,

• a pressure of the plasma and

• a power density of the plasma,

and the power emitted as a function of time is adapted according to at least one of these parameters;

- the plasma is contained in a cavity with at least one of the following properties:

• the pulsed discharge has a peak power of at least 5 kW at 2.45 GHz,

• the pressure of the plasma is between 100 mbar and 350 mbar and

• the gas containing hydrogen and carbon is emitted with a ratio of the flow rate to the volume of the plasma of between 0.75 and 7.5 sccm/cm³;

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- the plasma is contained in a cavity with at least one of the following properties:

- the pulsed discharge has a peak power of at least 10 kW at 915 MHz,

5 · the pressure of the plasma is between 100 mbar and 350 mbar and

- the gas containing hydrogen and carbon is emitted with a ratio of the flow rate to the volume of the plasma of between 0.75 and 7.5 sccm/cm³.

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Other aspects, objects and advantages of the invention will become apparent on reading the description of one of its embodiments which is given as a non-limiting example.

15

The invention will also be more clearly understood from the drawings, in which:

- Figure 1 shows one embodiment of the method according to the invention; and

20 - Figures 2a and 2b are graphs showing a pulsed discharge according to the invention.

In the various figures, the same references denote identical or similar elements.

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Figure 1 shows an example of how to implement the method according to the invention using a vacuum chamber 1 containing a support 2 placed on its base 3. This vacuum chamber is placed in a Faraday cage 13 acting as cavity or the vacuum chamber itself acts as cavity. Also in the vacuum chamber is a single injection nozzle 4, or a plurality of injection nozzles, for emitting into the vacuum chamber, gases comprising, on the one hand, a source of molecular hydrogen, such as dihydrogen H₂, and, on the other hand, a source of carbon, such as for example a hydrocarbon like methane CH₄, carbon dioxide CO₂ or the like.

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Controlled amounts of argon (Ar) or of dopants and impurities, such as boron (B), sulphur (S), phosphorus (P) or other dopants, may furthermore be emitted by the injection nozzle 4.

5

Positioned on the support 2 is a substrate 5, which for example may be a single-crystal or polycrystalline, natural or synthetic, diamond substrate, or even a non-diamond substrate, such as a silicon substrate, whether
10 biased or not, an SiC substrate or an iridium or platinum substrate for example.

The gases emitted by the injection nozzle 4 expand into the vacuum chamber and are exposed to a discharge
15 generated by a microwave generator 6 such as a GE 60KEDC SAIREM microwave generator operating at 2.45 GHz or a microwave generator operating at 915 MHz, the microwaves being guided by a waveguide 14. This discharge is coupled to the cavity 13 in such a way
20 that the gases form, around the substrate 5, a plasma 7 comprising, apart from the molecules of the gases:

- hydrogen atoms H and
- carbon-containing radicals, for example those in the form of CH_3 , and in general in the form of C_xH_y or
25 the like.

The plasma 7 may adopt an almost hemispherical shape, for example with a diameter of between 5 cm and 10 cm or other, about the substrate 5. The carbon atoms
30 contained in the plasma 7 are deposited on the substrate 5 and form a diamond film 8.

The substrate 5 and the diamond film 8 are heated by the surrounding plasma 7 up to a substrate temperature
35 T_s of around 700°C to 1000°C . Furthermore, the temperature of the substrate and of the film may be regulated by a regulating device (not shown) suitable for heating and/or cooling the substrate, this device being contained for example in the support 3. This

makes it possible, during implementation of the method, to decouple the injected power parameters from the substrate temperature parameters.

- 5 The power generated by the microwave generator 6 is illustrated in Figure 2a. This power is periodic with time and has, over a period T :
- a peak power P_c for a heating time T_{on} and then
 - a low power, relative to the high power, which
- 10 might be almost zero, for a standby time T_{off} .

The signal is not necessarily strictly periodic during the method, and the durations of the heating and standby times T_{on} and T_{off} may vary, for example

15 depending on the conditions measured in the plasma.

Likewise, the emitted power is not necessarily a square wave. For any periodic signal, it is possible, over a period, to calculate the mean P_m of the emitted power.

20 The emitted power greater than the mean power defines the heating time T_{on} and is called hereafter the "high power". The high power has a maximum instantaneous value called the "peak power" P_c . The emitted power less than the mean power defines the standby time T_{off}

25 and is called hereafter the "low power". The times T_{on} and T_{off} are optionally fractionated over a period.

Within the context of the invention, the peak power P_c may have a value of between 5 kW and 60 kW.

30

The duty cycle of the microwave generator 6, equal to the ratio of the heating time T_{on} to the period $T = T_{on} + T_{off}$, is between 10% and 50%. Thus, the ratio of the time when high power is emitted to the time when

35 low power is emitted may be between 1/9 and 1.

Apart from in a transient regime at the start of the heating time T_{on} , having a duration much less than T_{on} , during which the plasma volume varies, principally

increasing, the plasma has during the heating time T_{on} a generally constant volume directly related to the pressure of the plasma, which in practice is between approximately 100 mbar and 350 mbar, and to the
5 microwave frequency of the microwave generator used. The rest of the description ignores the transient state occurring at the start of the heating time, taking into account only the "steady state" of the plasma that occurs thereafter.

10

Such a periodic pulsed discharge is used to obtain a pulsed plasma whose temperature remains high, thereby guaranteeing high concentrations of hydrogen atoms H and carbon-containing radicals and therefore a high
15 deposition rate, while maintaining a low temperature of the walls 13 of the vacuum chamber 1. With such an absorbed power, the temperature of the plasma 7 rises up to a maximum value of between 3500 K and 5000 K. Consequently, and depending on the volume of the plasma
20 7, the power density corresponding to the peak power injected into the plasma is between 100 W/cm^3 and 250 W/cm^3 . This power density is calculated as the ratio of the peak power P_c to the volume of the plasma 7, which may be measured by specific measurement means
25 such as, for example, optical spectroscopy, or by a high-speed optical camera of the "Flash Cam" type, for example in the visible range, or by other means. The gas temperature in a boundary region of the plasma, located less than 1 cm from the surface of the
30 substrate, between the substrate and the generator, may also be between 1500 K and 3000 K.

These conditions greatly favour the disruption of the molecular hydrogen H_2 emitted by the injection nozzle 4
35 and the formation of carbon-containing radicals. A concentration of atomic hydrogen in the plasma of between $1.7 \times 10^{16} \text{ cm}^{-3}$ and $5 \times 10^{17} \text{ cm}^{-3}$ may be measured. Such an atomic hydrogen concentration makes it possible to increase the reaction rate for depositing the

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carbon-containing radicals contained in the plasma in the form of diamond to a high reaction rate, while guaranteeing the electronic quality of the diamond film produced. These conditions thus advantageously allow
5 the concentration of carbon-containing radicals in the plasma to be increased so that the latter may contain between $2 \times 10^{14} \text{ cm}^{-3}$ and $1 \times 10^{15} \text{ cm}^{-3}$ CH_3 radicals. Since the incorporation of carbon atoms into the diamond film
8 being formed is substantial, the molecular methane
10 may be emitted by the injection nozzle 4 with a molar ratio with respect to molecular hydrogen H_2 of possibly up to 12%.

In the considered embodiment, the volume of the plasma
15 is kept overall constant at 65 cm^3 by a flow via the injection nozzle 4 with a flow rate of between 50 sccm and 500 sccm, which corresponds to a ratio of the flow rate to the volume of plasma of between 0.75 and 7.5
sccm/ cm^3 for example. Of course, it is unnecessary for
20 the plasma to maintain a constant volume during the method, nor indeed does this volume have to be around 65 cm^3 . The volume of the plasma may be modified by regulating its pressure within the 100 mbar - 350 mbar range. Furthermore, the volume of the plasma may also
25 be increased or reduced by using a microwave generator at a lower or higher microwave frequency respectively.

As explained above, using a controlled pulsed discharge allows the characteristics of the plasma to be
30 increased, in particular the atomic hydrogen and carbon-containing radical concentrations therein, since the temperature of the plasma can be increased while the wall temperature, directly related to the mean power of the discharge, remains low. The significant
35 parameters governing the growth of the diamond film are thus directly related to the peak power.

Thus, by reducing the heating time T_{on} for a given period, and for a given mean power, the peak power P_c

may be increased up to maximum values ranging from 6 kW to 60 kW, depending on the generator used. The reaction rate is related to the concentration of atomic hydrogen and of carbon-containing radicals in the plasma 7 and by the temperature of the substrate T_s . On the other hand, the mean power of the discharge cycle must remain low so as to avoid an excessively high temperature of the walls 13 of the vacuum chamber 1, which leads, for a constant period T of the discharge cycle, to reducing the heating time T_{on} and increasing the standby time T_{off} . During that part of the discharge cycle between T_{on} and T , a low, even zero, microwave power is injected into the plasma 7 so that the radicals in this plasma recombine. Thus, the concentration of atomic hydrogen H in the plasma 7 decreases during this time interval and the atoms recombine into hydrogen molecules H_2 , which again will have to be disrupted during the next discharge, thereby reducing the efficiency of the process. During the standby time T_{off} , the atomic hydrogen concentration decreases with time, characterized by a lifetime T_v of the hydrogen atoms in the plasma that depends on the temperature and pressure conditions of the plasma. It is desirable to try to limit the process of hydrogen atoms recombining during the standby time T_{off} so as to have to disrupt the minimum amount of hydrogen molecules H_2 during the next heating time T_{on} .

The invention makes it possible to obtain a pulsed microwave plasma using an energy source 6 delivering a periodic discharge with time, the standby time T_{off} of which is strictly shorter than the lifetime T_v of the hydrogen atoms in the plasma 7.

The lifetime T_v of the atomic hydrogen H in the plasma 7 may be determined, for example, by a known plasma induced fluorescence (PIF) technique consisting in generating, as shown in Figure 2b, in addition to the first power peak of duration T_{on} , with a peak power P_c a

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second power peak, after the first, at a defined time T_0 taken between T_{on} and T and of short duration, for example about $1/10$ of T_{on} , which, by direct collision with an electron, excites the hydrogen atoms H still present in the plasma 7 at time T_0 , this excitation being measured and compared with the excitation caused by the first peak of the discharge, thereby making it possible to determine the concentration of hydrogen atoms H remaining in the plasma 7 at time T_0 and therefore the hydrogen atom lifetime under the given conditions of the plasma. Optionally, this information may be transmitted to the microwave generator 6 which adapts the parameters of the discharge accordingly. Other known techniques, such as laser-induced stimulated emission (LISE) or two photon laser-induced fluorescence may be used in this context.

Measures may also be taken to ensure that, during the standby time T_{off} , a residual power P_R of about 10% of the peak power P_c is injected into the plasma so that the microwave generator 6 remains active and can deliver more rapidly, at the start of each new discharge cycle period, a high peak power P_c .

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CLAIMS

1. Method for manufacturing a diamond film (8) using
a pulsed microwave plasma, in which, in a vacuum
5 chamber (1), a plasma (7) of finite volume is formed
near a substrate (5) by subjecting a gas containing at
least hydrogen and carbon to a pulsed discharge, which
has a succession of low-power states and high-power
states, and having a peak absorbed power P_c , so as to
10 obtain at least carbon-containing radicals in the
plasma (7) and to deposit the said carbon-containing
radicals on the substrate (5) in order to form a
diamond film (8) thereon;
characterized in that power is injected into the volume
15 of the plasma with a peak power density of at least
 100 W/cm^3 while maintaining the substrate (5) to a
substrate temperature of between 700°C and 1000°C .

2. Method according to Claim 1, in which a plasma (7)
20 having at least one of the following features is
generated near the substrate (5):

- the pulsed discharge has a certain peak
absorbed power P_c and the ratio of the peak power to
the volume of the plasma is between 100 W/cm^3 and
25 250 W/cm^3 ,

- the maximum temperature of the plasma is
between 3500 K and 5000 K,

- the temperature of the plasma in a boundary
region of the plasma located less than 1 cm from the
30 surface of the substrate is between 1500 K and 3000 K
and

- the plasma contains hydrogen atoms having a
maximum concentration in the plasma of between 1.7×10^{16}
and $5 \times 10^{17} \text{ cm}^{-3}$.

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3. Method according to Claim 1 or Claim 2, in which
said gas contains carbon and hydrogen in a
carbon/hydrogen molar ratio of between 1% and 12%.

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4. Method according to any one of the preceding claims, in which said gas contains at least one hydrocarbon, and a plasma (7) having a concentration of the carbon-containing radicals of between $2 \times 10^{14} \text{ cm}^{-3}$ and $1 \times 10^{15} \text{ cm}^{-3}$ is generated.

5. Method according to any one of the preceding claims, in which a pulsed discharge is produced, in which the ratio of the duration of the high-power state to the duration of the low-power state is between 1/9 and 1.

6. Method according to any one of the preceding claims, in which at least one of the following parameters is estimated:

- a substrate temperature,
 - a temperature of the plasma,
 - a temperature of the plasma in said boundary region, located less than 1 cm from the surface of the substrate,
 - a concentration of atomic hydrogen in the plasma,
 - a concentration of carbon-containing radicals in the plasma,
 - a concentration of carbon-containing radicals in said boundary region close to the plasma,
 - a pressure of the plasma and
 - a power density of the plasma,
- and the power emitted as a function of time is adapted according to at least one of these parameters.

7. Method according to any one of the preceding claims, in which the plasma is contained in a cavity (13) with at least one of the following properties:

- the pulsed discharge has a peak power of at least 5 kW at 2.45 GHz,
- the pressure of the plasma is between 100 mbar and 350 mbar and

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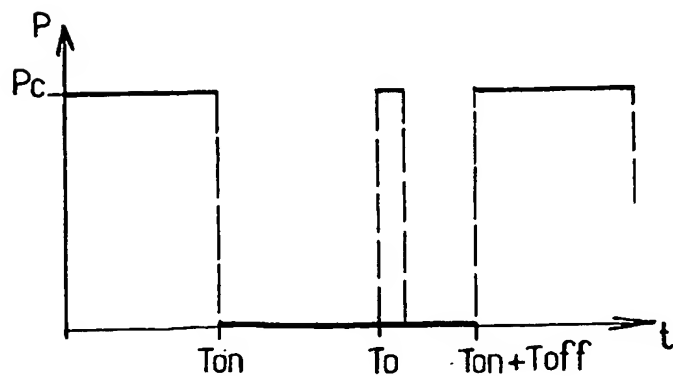
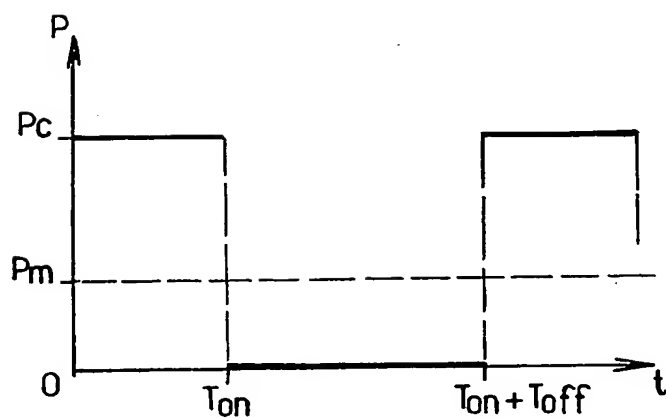
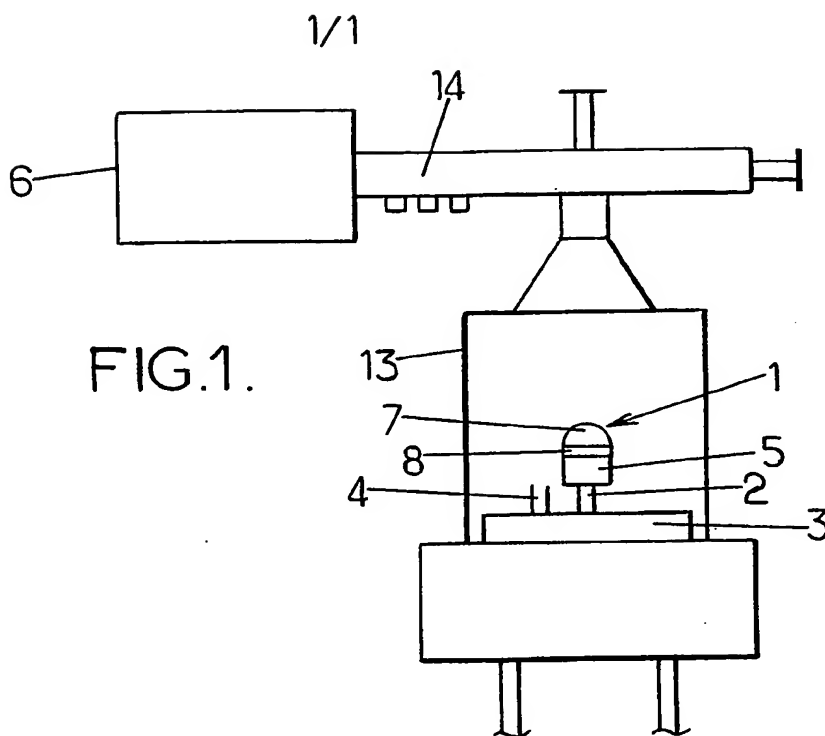
· the gas containing hydrogen and carbon is emitted with a ratio of the flow rate to the volume of the plasma of between 0.75 and 7.5 sccm/cm³.

- 5 8. Method according to any one of Claims 1 to 6, in which the plasma is contained in a cavity with at least one of the following properties:

· the pulsed discharge has a peak power of at least 10 kW at 915 MHz,

- 10 · the pressure of the plasma is between 100 mbar and 350 mbar and

· the gas containing hydrogen and carbon is emitted with a ratio of the flow rate to the volume of the plasma of between 0.75 and 7.5 sccm/cm³.



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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C30B25/10 C30B25/02 C30B29/04 C23C16/27 C23C16/511
C23C16/515

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C30B C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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